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Dispersion analysis of nano-particles in polymers by SAXS

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Introduction

Polymer composites with inorganic materials having both flexibility of polymers and thermal stability of inorganic materials are used in many industrial fields. In recent years, the polymer composites with nano-particles are paid attentions as performance materials. The properties of polymer/nano-particles composites such as mechanical and thermal stability etc. are influenced by the dispersion state of nano-particles in the polymer matrix. In this study, the dispersion of nano-particles (SiO_2) in poly(methyl methacrylates) PMMA was investigated by SAXS.

Experiments

Nano-composites of PMMA and SiO_2 were prepared by casting from THF solution, which was good solvent for PMA esters and allowed homogeneous dispersion of SiO_2 nano-particales. SiO_2 with the diameter of 13, 17, 23 nm were dispersed into PMMA. The SiO_2 weight fraction to PMA esters was varied from 0 to 20 wt%.

Small-angle X-ray scattering (SAXS) experiments of PMMA and PMMA-SiO_2 composites were performed at 25 °C using the SAXS optics at the beam line 10C, Photon Factory, High Energy Accelerator Research Organization, Tsukuba, Japan. The wavelength of X-ray (λ) used was 0.15 nm. The accumulation time of SAXS measurement was 300 sec. The scattering vector ($q = (4\pi \sin\theta)/\lambda$) covered from 0.02 to 5 nm^{-1}, 2θ was the scattering angle.

Results

The normalized SAXS profiles of PMMA and PMMA-SiO_2 composites (17 nm) were shown in Fig.1. The SAXS profiles of PMMA-SiO_2 composites showed the scattering peaks at q = 0.2 and 0.9 nm^{-1}. The observed SAXS profile, $I(q)_{obs}$, was described as follows.

$$I(q)_{obs} = I(q)_{PMMA} + I(q)_{SiO2} \quad (1)$$

Here, $I(q)_{PMMA}$ and $I(q)_{SiO2}$ indicate SAXS profiles from PMMA and SiO_2, respectively. From the X-ray scattering theory [9], $I(q)_{SiO2}$ is evaluated by the following equation.

$$I(q)_{SiO2} = n_p \int_0^\infty P(q,R) S(q,R_{eff}) f(R) dR \quad (2)$$

Here, n_p, R, $P(q,R)$, $S(q,R)$ and $f(R)$ are the average number density of particles, the radius of particle, the form factor, the structure factor of system and the distribution of particles, respectively.

$$P(q)_{SiO2} = \left[(\rho_{SiO2} - \rho_{PMMA})(R_{SiO2})^3 F(q,R_{SiO2})\right]^2 \quad (3)$$

$$F(q,R_{SiO2}) = 3\left\{\left[\sin(qR_i) - (qR_i)\cos(qR_i)\right]/(qR_i)^3\right\} \quad (4)$$

Here, ρ_i indicates the scattering electron density of PMMA and SiO_2.

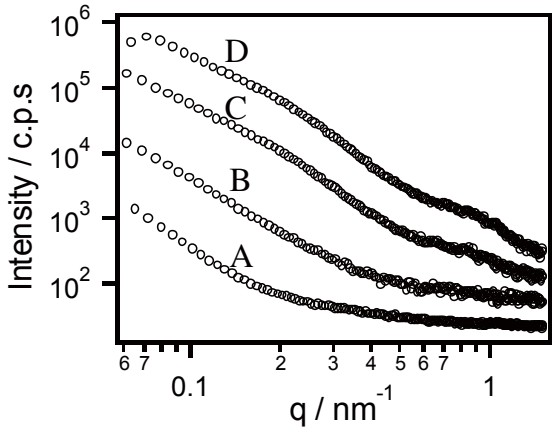

Fig1. SAXS profiles of PMMA and PMMA-SiO_2 (17 nm) composites with various mass fraction of SiO_2 (A: PMMA, B: 1 %, C: 4 %, D: 15 %).

The SAXS profile fitting was carried out using equation (2) to evaluate the dispersion state and the diameter of SiO_2 particles. The obtained diameter of SiO_2 particle was 16 nm for PMMA-SiO_2 composites (17 nm) with 4 and 15 wt% of ϕ_{SiO_2} under the condition of fixed $f(R) = 0.1$. These results indicated that SiO_2 particles dispersed homogeneously in PMMA in the ϕ_{SiO_2} range below 15 wt%. The SAXS profile of PMMA-SiO_2 composite with 15 wt% accompanied the scattering at lower q region, which indicated the existence of SiO_2 aggregation. PMMA-SiO_2 composites with ϕ_{SiO_2} below 10 wt% were optically transparent, however, the composites became opaque with the increase of ϕ_{SiO_2} above 15 wt% as a result of particle aggregation.

References

[1] D. Q. Zou , H. Yoshida, *J Therm Anal Calorim* , 99:21–26(2010)

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